Research papers

An experimental examination of the effect of the salt type on the chemo-osmotic, diffusive, and hydraulic parameters of Wakkanai mudstones

Mitsuo Manaka*, Mikio Takeda

Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

ABSTRACT

To better understand the groundwater flow and chemistry in argillaceous formations, the dependency of transport parameters such as permeability, diffusion coefficient, and chemical osmotic efficiency on each of the chemical species dominant in groundwater must also be understood. Despite its importance, however, little is known about the dependence of transport parameters on different types of groundwater. Thus, we investigated transport parameters of Wakkanai mudstones using three different types of electrolyte solutions. Here, we report the relationship among the solution salt type, solute concentration, transport parameters, and pore structure characteristics. Wide ranges in osmotic efficiency and intrinsic permeability, 0.0035–0.14 and 1.19×10^{-19} to $4.75 \times 10^{-18}\,\mathrm{m^2}$, respectively, reflect the difference in the solution composition based on the salt type, difference in solute concentration, and variation in the pore size distributions of Wakkanai mudstones. The effective diffusion coefficients with filtration effects, at 2.98×10^{-11} to $5.92 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$, vary depending on salt type, but remain invariant among samples, indicating no difference in fluid flow path associated with small values of osmotic efficiency. In contrast, the osmotic efficiencies are related to differences in salt concentrations. Our findings indicate that salt concentration and pore structure characteristics determine not only the semipermeability of the Wakkanai mudstones but also the diffusivity and permeability.

1. Introduction

The complex hydrogeologic properties of argillite include membrane behavior, which affects semipermeability and induces chemical osmosis under a salinity gradient. Thus, the groundwater flow system in an argillaceous formation is governed by not only topography- and pressure-driven flow but also by flow driven by chemical osmosis- and thermo-osmosis- (Gonçalvès et al., 2004, 2010, 2012; Neuzil, 2000, 2013; Wilson et al., 2003). Chemical osmosis involves flow from low to high concentration zones. Essentially, this process describes water migration through a semipermeable membrane driven by differences in the chemical potential of the water migrating across the membrane, which continues until the difference in potential energy is compensated by other potential differences such as the pressure difference (e.g., Mitchell and Soga, 2005). Assuming that a salinity gradient exists in a formation and that the formation behaves as a semipermeable membrane, chemical osmosis may generate abnormal pressures and hydraulic head profiles, which could persist for tens of millions of years (e.g., Neuzil, 2000; 2015). The occurrence of large erratic pressures has been re-examined by Neuzil and Provost (2009) and was discussed in Tremosa et al. (2012). Therefore, the possibility of chemical osmosis in

groundwater systems of sedimentary formations should be carefully examined.

Chemical osmosis depends on the clay mineralogy, porewater chemistry, and pore size distribution of a sedimentary formation (e.g., Bresler, 1973; Gonçalvès et al., 2007; Leroy and Revil, 2004; Neuzil, 2000; Rahman et al., 2005; Takeda et al., 2014). For example, clay minerals have a negative surface charge, and their surfaces generate electrical double layers (EDLs; e.g., Appelo and Postma, 2005). When the pore space between two clay particles is small and the EDLs overlap, repulsion occurs. Electrical repulsive forces generated by a negative potential field inhibit anions via migration through the pore. The passage of anions is restricted when compaction decreases the pore size so that the diffuse double layers of two clay particles overlap to cause anion exclusion. The distribution of electrical charges in solution enables transport of water and non-charged solutes but restricts the passage of charged species through the pore network, which is related to the semi-permeable membrane behavior of the clay. In such media, osmosis can cause fluid to flow from regions of low salt concentration to those of high salt concentration, where a fluid pressure build up is induced. The solute concentration and ionic composition of the groundwater affect the EDLs on the surface of clay minerals. The groundwater

---

contains solutes with different electric charges and concentrations. In addition, the solutes may be spatially unevenly distributed owing to the groundwater flow system during sedimentation. This means that various porewater solutes can lead to cation exchanges within the EDLs at the clay mineral surface. Correspondingly, chemical osmosis depends on the porewater chemistry. Therefore, to evaluate chemical osmosis in sedimentary formations, it is necessary to determine how the differences in groundwater solutes affect this osmosis. Apart from the electrical characteristics of clay mineral surfaces, the pore size distribution affects chemical osmosis: When the dominant interconnected pore space is narrow, the pore throats available for fluid flow enhance the semipermeable membrane behavior.

The effect of semipermeability on rocks has been investigated in several previous studies (e.g., Cey et al., 2001; Horseman et al., 2007; Neuzil, 2000; Rousseau-Gueutin et al., 2010; Takeda et al., 2014). In most of these studies, differences in NaCl salt concentration were identified as driving forces of chemical osmosis. However, the effect of the salt type on the chemical osmosis of rocks has been discussed only by Al-Bazali et al. (2005), Neuzil and Person (2017), Tremosa et al. (2012), and Villabona-Camacho et al. (2009). These authors used the same rocks for NaCl, KCl, and $CaCl_2$ solutions. They observed variation in the osmotic efficiency values, which is a parameter of semipermeability ranging from 0 (non-membrane) to 1 (perfect membrane), and explained this effect by discussing the difference in mobility of these electrolytes. Monovalent sodium and potassium ions with small ionic radii have a higher mobility than divalent calcium ions. In contrast, many studies reported the effects of different salts and concentrations on the semipermeability of clay membranes consisting of different clay types such as undisturbed natural clay rocks and remolded pure clays. The salts that were used in the previous research include NaCl (Hart et al., 2008; Noy et al., 2004; Rousseau-Gueutin et al., 2008), KCl (Cheng and Hendry, 2014; Kang and Shackelford, 2011; Malusis and Shackelford, 2002; Tang et al., 2014, 2015), $NaHCO_3$ (Garavito et al., 2007), $NaNO_3$ (Derrington et al., 2006), and $NaPO_4$ (Derrington et al., 2006). These results can be summarized as follows. The osmotic efficiency decreases when the solute concentration increases, and increases in the concentration cause a progressively greater shrinkage of the EDLs of the clay particles. In addition, the charge of the clay surface is equal and opposite to the charge of the double layer, which is distributed depending on the solute concentration of the solution. Cations and anions closer to the surface with increasing solute concentration balance the surface charge; thus, the double layer becomes thin (thick) at high (low) solute concentration. A high concentration yields a highly accessible porosity for ionic transport and a leaky membrane corresponding to osmotic efficiency values close to zero. Moreover, the osmotic efficiencies of the cation or anion species differ according to the different interactions between the solutes and the mineral surfaces.

Therefore, the salt type and concentration affect the semipermeability of geologic media. Similarly, the type and concentration of the salt and porosity affect the permeability of geologic media (e.g., Cey et al., 2001; Mesri and Olson, 1971). Mesri and Olson (1971) reported the variation in permeability values using smectite, illite, and kaolinite (pure clays) for NaCl or $CaCl_2$ solutions with different concentrations and void ratio values. They attributed this variation to the tendency of clay to disperse or form aggregates. Dispersion reduces fluid flow because it creates flow channels with nearly the same size, and aggregation tends to increase fluid flow owing to the existence of many small flow channels and a relatively smaller number of main flow channels. Cey et al. (2001) reported that the hydraulic conductivity of a natural clay- rock increases with an increase in pore fluid concentration, which can be explained by the diffuse double-layer theory. These studies suggest that the type and concentration of salt in porewater (or groundwater) and the pore structure of geologic media affect the transport parameters through their influence on the media parameters such as microstructure and EDL. Despite its importance, however, the relationship between the salt type, solute concentration, and transport

parameters in undisturbed rocks has not been fully examined from an experimental standpoint.

This study focuses on the effect of different salt types and concentrations on the transport parameters of Wakkanai mudstones. These mudstones were previously studied by Takeda et al. (2014), who estimated the semipermeability, permeability, and diffusion coefficient based on NaCl solution. In the present study, we performed permeability and chemical osmosis experiments on the same mudstone samples by using KCl and $KHCO_3$ solutions to determine the relationship between the salt type and the transport parameters. The use of the same samples is expected to have better results in the comparison of transport parameters. As salt types, KCl, $KHCO_3$, and NaCl were selected based on the sensitivity of chemical osmosis of 1:1 electrolytes compared with solutions of ionic species with different valences. The groundwater in this area has a NaCl-dominated water chemistry at depths below 250 m and an increase in water salinity with depth, showing that the second most common cation and anion are K^+ and HCO_3^-, respectively, and that the content of divalent species is limited (Hama et al., 2007). In addition, the selection of divalent species is expected to cause difficulty in the experimental observation of chemical osmosis because it reduces the osmotic efficiency (e.g., Tremosa et al., 2012). Thus, this study explores the relationship among the three aforementioned salt types, the transport parameters, and the pore structures of Wakkanai mudstones. Sequential permeability and chemical osmosis experiments based on the study by Takeda et al. (2014) are conducted to examine the chemo-osmotic, hydraulic, and diffusion parameters as transport parameters for each rock sample. The hydraulic parameters are estimated from the permeability experiments, and the chemo-osmotic and diffusion parameters were estimated from the chemical osmosis experiments. Based on the experimental results, the effects of salt type and of various KCl concentrations are discussed with respect to these three parameters for each rock sample. Moreover, these transport parameters are discussed with respect to the pore structures of the rock samples.

2. Experimental materials and methods

2.1. Materials

The samples are argillaceous rocks that were retrieved from boreholes HDB-9 and HDB-11 drilled in the marine Wakkanai Formation in the Horonobe area of Japan. Takeda et al. (2014) previously extracted disc-shaped rock samples 50 mm in diameter and 10 mm in thickness from the 80-mm-diameter cores of these boreholes and performed experiments. We used the same samples in the present experiment. Carefully observation by the unaided eye revealed no fissures or fractures in these samples. The average pore radius, porosity, specific surface area, cation exchange capacity, and pore structure of the core samples are summarized in Table 1. The porosity and average pore radius of the cores differ only slightly, although the pore structure characteristics depend on the pore size distribution. The pore size distribution revealed the presence of three groups of pore structures in these samples. The first group is sample No. 2, which has a distinct bimodal distribution with peaks centered at ~4–5 nm and 10–30 nm. The second group consists of samples Nos 1 and 3, which have a slight bimodal distribution with peaks centered at ~7–8 nm and 10–20 nm. The third group is composed of sample Nos. 4 and 5, which show a clear peak at ~8 nm. The pore structures of the cores were characterized on the basis of different pore size distributions of pores with sizes greater than 10 nm: (1) nanoscale pores < 10 nm, accounting for 56%–67% of the total pore space, (2) 10–100 nm, accounting for 40%–30% of the total pore space.

Bulk rock powders were analyzed by using an X-ray powder diffractometer (RINT2500, Rigaku) using monochromatic CuKα radiation at 40 kV and 100 mA from 2.5° to 70°. The step size was 0.02°, and the scan speed was 2° min^{-1}. The clay fractions (< 2 μm) of the mudstones were extracted by using a conventional sedimentation method